

(19)



Europäisches Patentamt
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(11)

EP 0 952 142 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
27.10.1999 Bulletin 1999/43

(51) Int Cl. 6: C07C 69/007, C07C 69/96,
A61K 7/32, A61K 7/46

(21) Application number: 99810249.5

(22) Date of filing: 22.03.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 20.04.1998 EP 98810337

(71) Applicant: Givaudan Roure (International) S.A.
1214 Vernier-Genève (CH)

(72) Inventors:

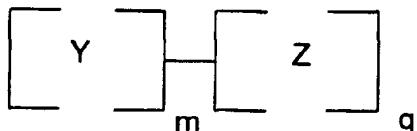
• Anderson, Denise, Dr.
8032 Zürich (CH)

- Frater, Georg, Dr.
8400 Winterthur (CH)
- Kumli, Frank, Dr.
8600 Dübendorf (CH)

(74) Representative: Patentanwälte
Schaad, Balass, Menzl & Partner AG
Dufourstrasse 101
Postfach
8034 Zürich (CH)

(54) Compounds with protected hydroxy groups

(57) Compounds with protected hydroxy groups of formula I



are precursors for organoleptic compounds such as fragrances and masking agents and for antimicrobial compounds. The symbols in formula I are defined in claim 1. Upon activating conditions, the compounds of formula I are cleaved and yield one or more organoleptic or antimicrobial compounds.

Description

[0001] The present invention relates to a new group of compounds with protected hydroxy groups which are precursors for organoleptic compounds (such as fragrances and masking agents) and antimicrobial compounds.

[0002] A principal strategy currently employed in imparting odours to consumer products is the admixing of the fragrance directly into the product. There are, however, several drawbacks to this strategy. The fragrance material can be too volatile, resulting in fragrance loss during manufacturing, storage, and use. Many fragrance materials are also unstable over time. This again results in loss during storage.

[0003] In many consumer products it is desirable for the fragrance to be released slowly over time. Microencapsulation and inclusion complexes with cyclodextrins have been used to help decrease volatility, improve stability and provide slow-release properties. However, these methods are for a number of reasons often not successful. In addition, cyclodextrins can be too expensive.

[0004] Fragrance precursors for scenting fabrics being washed in the presence of lipase-containing detergents are described in WO 95/04809. The fragrance precursors contained in the detergent and/or in the softener are cleaved by the lipase and a single odoriferous compound, either an odoriferous alcohol or aldehyde or ketone is yielded. Thereby a prolonged scenting effect on the fabric is obtained.

[0005] One object of the present invention is to provide new precursors for compounds with different activities.

[0006] It is a preferred object of the present invention to provide compounds cleaved under different activating conditions.

[0007] A further object of the invention is to provide new compounds which are stable under transport and storage conditions.

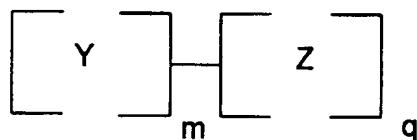
[0008] A further object of the present invention is to provide precursor molecules supplying different active compounds simultaneously or successively.

[0009] The present invention relates to compounds of formula I

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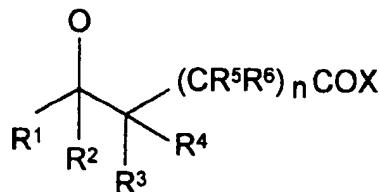
I

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35 wherein Y is

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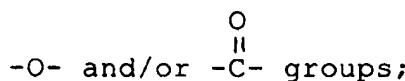


45 m is an integer of 1 or greater

n is 1, 2 or 3;

50 R¹, R², R³, R⁴, R⁵ and R⁶ represent independently hydrogen, substituted or unsubstituted alkyl-, alkenyl-, alkinyl-, cycloalkyl-, cycloalkenyl- or aromatic radicals which can additionally contain one or more

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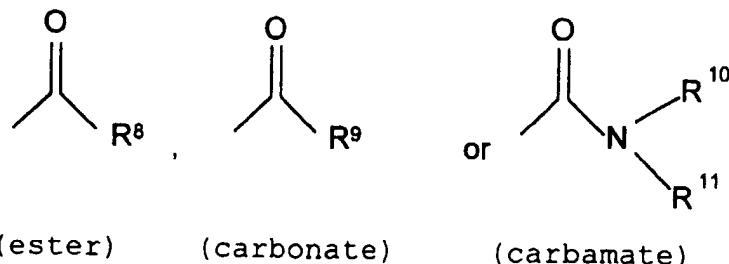
whereby one or two rings can be built by the combination of the respective R¹ to R⁶ and said ring(s) can be substituted by one or more alkyl group;

X is -OR⁷ and R⁷ is the residue of an alcohol R⁷OH, or the residue of the enol form of an aldehyde or ketone, or X is a primary, or secondary amino group forming an amide;

Z is

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q is the same or bigger than m;

20 R⁸ represents hydrogen, a straight or branched, unsubstituted or substituted alkyl-, alkenyl-, cycloalkyl-, cycloalkenyl- or aromatic radical which optionally comprises and/or is substituted by one or more heteroatoms, and/or group(s) comprising a heteroatom preferably by -CO-, OCOR⁷, COOR⁷, COY, Si and/or N;

25 R⁹ is the residue -OR¹² of an alcohol of formula R¹²OH or the residue of the enol form of an aldehyde or ketone or has the definition given for Y and R⁹ and Y can be the same or different and optionally comprises and/or is substituted by a heteroatom, and/or group(s) comprising a heteroatom;

30 R¹⁰ and R¹¹ represent independently hydrogen, substituted or unsubstituted alkyl, alkenyl, cycloalkyl, cycloalkenyl or an aromatic residue which optionally comprise and/or are substituted by one or more heteroatoms, and/or group(s) comprising a heteroatom preferred heteroatoms and groups with heteroatoms for R⁹, R¹⁰ and R¹¹ are O, Si, N and CO.

35 [0010] Further characteristics and advantages of the invention are described by claims 2 to 11 and by the following specification and examples.

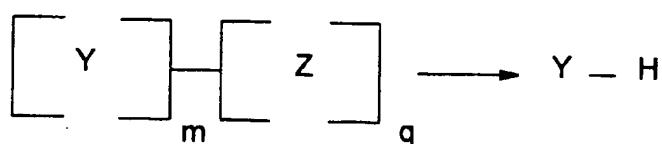
[0011] The compounds of formula I are not limited to any particular stereoisomers, all possible stereoisomers (E/Z isomers, enantiomers, diastereomers) and all mixtures are thus included within the scope of the invention.

[0012] The compounds of formula I are virtually odourless under room temperature, atmospheric conditions and about 20 to 100% relative humidity. However, under activating conditions, they are cleaved and one or more active compounds with organoleptic and/or antimicrobial properties are generated.

[0013] The activating conditions which lead to cleavage and the desired active compounds comprise the presence of skin bacteria, especially axilla bacteria, of an enzyme such as protease or lipase, elevated temperature or acidic or alkaline pH-values and/or light. The compounds of formula I, upon cleavage, provide lactones and optionally aldehydes, ketones, and/or alcohols having organoleptic and/or antimicrobial activity and therefore permit the development of useful consumer products with enhanced organoleptic and/or microbiological properties. Further, the compounds of formula I, upon cleavage can generate fluorescent coumarins useful as optical brighteners.

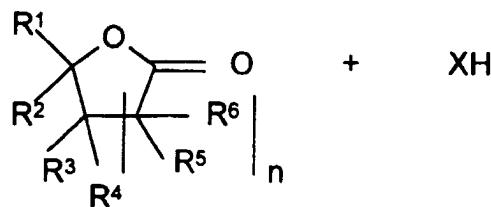
[0014] The compounds I of the present invention are cleaved in under activating conditions in two successive steps, first the „protective group„, Z is removed resulting in a hydroxyester

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which decomposes into one or more organoleptic lactone(s), and one or more alcohol (s), amine(s), aldehyde (s) and/or ketone(s).



[0015] Z may be considered a protective group which prevents the hydroxy ester Y-H from premature cyclisation to an organoleptic lactone. At the same time Z can generate one or more additional organoleptic compound(s). In the following, cleavage of a β -ketoester of formula I is shown.

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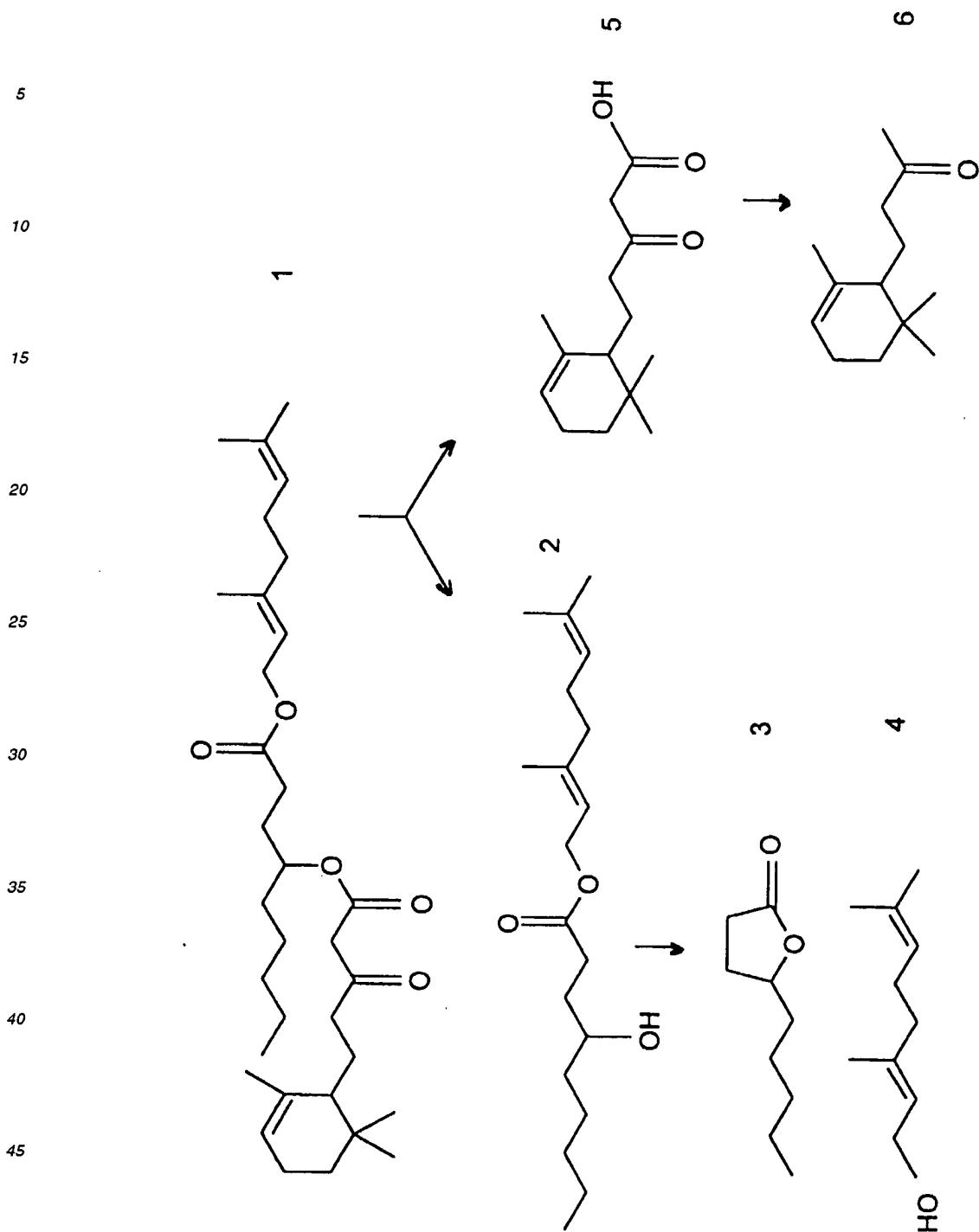
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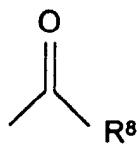
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[0016] Thus one compound of formula I can yield under activating conditions three different organoleptic compounds.

[0017] If Z is

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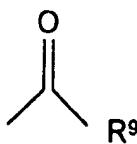
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it stands preferably for the residue of an odourless or antimicrobial acid optionally substituted by groups yielding upon cleavage one or more organoleptic compounds. Examples of esters in which R8 is an odourless acid are:

15 tetradecanoic acid 1-(2-hex-3-enyloxycarbonyl-ethyl)-heptyl ester;
 tetradecanoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxycarbonyl)-ethyl]-octyl ester;
 benzoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxycarbonyl)-ethyl]-octyl ester;
 dodecanoic acid 1-[2-(3,7-dimethyl-oct-6-enyloxycarbonyl)-ethyl]-heptyl ester;
 succinic acid 1-[2-(1,5-dimethyl-1-vinyl-hex-4-enyloxycarbonyl)-ethyl]-heptyl ester hex-3-enyl ester is a compound
 wherein R8 is COR7;
 20 succinic acid bis-{1-[2-(3,7-dimethyl-octa-2,6-dienyloxycarbonyl)-ethyl]-octyl} ester with R8 being COY.

[0018] If Z is

25



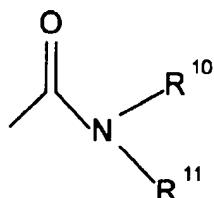
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[0019] R9 is preferably the residue of an organoleptic compound or Y. Examples of carbonates in which R9 is an organoleptic compound are:

35 4-phenethyloxycarbonyloxy-decanoic acid 3,7-dimethyl-oct-6-enyl-ester;
 4-phenethyloxycarbonyloxy-decanoic acid hex-3-enyl ester;
 4-hex-3-enyloxycarbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester;
 4-phenethyloxycarbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester;
 4-{1-[2-(1,1,5-trimethyl-hexyloxycarbonyl)-ethyl]octyloxycarbonyloxy}-decanoic acid 1,1,5-trimethyl-hexyl ester is
 40 a carbonate with R9 being Y.

[0020] If Z stands for

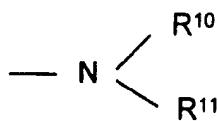
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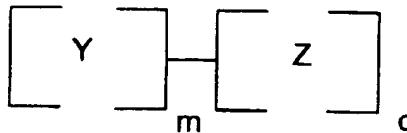
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is preferably derived from a non odorous mono- or diamine. 4- (Bis-decyl-carbamoyloxy)-undecanoic acid hex-3-enyl ester is such a preferred carbamate.

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can also be a photolabile ester.

20 [0021] The compounds of the present invention can act as fragrance precursors in personal care products, in laundry products, cleaning compositions, pet care products and environment scents such as air fresheners. They can also act as precursors for odour masking agents, e.g. in the same products as the fragrance precursors. They also can act as precursors for antimicrobial agents. The fragrance precursors and the precursors for odour masking agents of the invention may be used individually in an amount effective to enhance or to mask the characteristic odour of a material.

25 More commonly, however, the compounds are mixed with other fragrance components in an amount sufficient to provide the desired odour characteristics.

30 [0022] Due to the in situ generation of the active compounds the desired effect is prolonged and the substantivity on different substrates is enhanced. If two or more active compounds are provided, they can be generated, depending on the precursor and/or the activating conditions, simultaneously or successively. Further, the precursors of the invention provide slow release of the active compounds.

[0023] A broad range of known odorants or odorant mixtures can be generated from precursors of the invention.

[0024] Examples of aldehydes include:

35 2,6,10-trimethylundec-9-enal*
 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthalenecarboxaldehyde
 tridecanal
 2-[4-(1-methylethyl)phenyl]-ethanal
 2,4-dimethyl-cyclohex-3-ene-1-carbox-aldehyde*
 4-carboxaldehyde-1,3,5-trimethyl-cyclohex-1-ene*
 40 1-carboxaldehyde-2,4-dimethyl-cyclohex-3-ene*
 1-carboxaldehyde-4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene*
 3,5,5-trimethyl-hexanal
 heptanal*
 2,6-dimethyl-hept-5-enal*
 45 decanal**
 dec-9-enal
 dec-4-enal
 2-methyldecanal*
 undec-10-enal**
 50 undecanal*
 dodecanal**
 2-methyl-undecanal**
 tridecanal
 octanal**
 55 nonanal*
 3,5,5-trimethylhexanal
 undec-9-enal**
 2-phenyl-propanal*

4-methyl-phenyl-acetaldehyde*
 3,7-dimethyl-octanal*
 dihydrofarnesal**
 7-hydroxy-3,7-dimethyl-octanal*
 5 2, 6-dimethyl-oct-5-enal
 2-[4-(1-methylethyl) phenyl]-ethanal*
 3-(3-isopropyl-phenyl)-butanal**
 2-(3,7-dimethyoct-6-enoxy)-ethanal
 10 1-carboxaldehyde-4-(4-methyl-3-pentenyl)-cyclohex-3-ene*
 2,3,5,5-tetramethyl-hexanal
 longifolic aldehyde
 2-methyl-4-(2,6,6-trimethylcyclohex-2-en-1-yl)-butanal*
 2-methyl-3-(4-tert-butylphenyl)-propanal**
 15 4-(1,1-dimethyl-ethyl)-benzene-propanal*
 2-[4-(1-methylethyl)-phenyl]-propanal
 alpha-methyl-1,3-benzodioxole-5-propanal*
 3,7-dimethyl-oct-6-enal*
 20 2-methyl-3-(4-isopropylphenyl)-propionaldehyde*
 4-(4-hydroxy-4-methyl-pentyl)-cyclohex-3-en-1-carboxaldehyde**
 alpha-methyl-1,3-benzodioxole-5-propanal*
 1-carboxaldehyde-4-(1,1-dimethylethyl)-cyclohexane
 25 4-(octahydro-4,7-methano-5H-inden-5-ylidene)-butanal
 [(3,7-dimethyl-6-octenyl)-oxy]-acetaldehyde**
 hex-2-enal*
 2-nonenal*
 2-tridecenal*
 3,7-dimethyl-oct-2, 6-dien-1-al*
 2-nonadienal*
 2,4-dimethyl-2, 6-heptadienal
 30 trans-dec-2-en-1-al*
 2,4-diethyl-hep-2, 6-dien-1-al*
 dodec-2-en-1-al*
 3,7-dimethyl-oct-2, 6-dien-1-al*
 2,4-diethyl-hepta-2, 6-dienal
 35 3,7-dimethyl-nona-2, 6-dien-1-al*
 3-propyl-2-hepten-1-al
 1-carboxaldehyde-4-(prop-2-en-2-yl)-cyclohex-1-ene undecanal

whereby * indicates the preferred aldehydes and ** indicate the more preferred aldehydes.

40 [0025] Examples of ketones include:

2-heptyl-cyclopentanone
 2,2,6,10-tetramethyltricyclo-[5.4.0.0(6,10)]-undecan-4-one benzylacetone*
 carvone*;
 45 1,2,3,5,6,7-hexahydro-1,1,2,3,3,-pentamentyl-4H-inden-4-one*
 methyl heptenone*
 dimethyl octenone*
 2,5-dimethyl-oct-2-en-6-one**
 2-(butan-2-yl)-cyclohexanone*
 50 2-hexyl-cyclopent-2-en-1-one*
 2-(1-methylethyl)-5-methyl-cyclohexanone*
 2-(2-methylethyl)-5-methyl-cyclohexanone**
 3-methyl-cyclopentadecanone
 4-(1,1-dimethylpropyl)pentyl-cyclohexanone*
 55 4-tert-pentyl-cyclohexanone*
 2-oxo-1-pentyl-cyclopentane-acetic acid methyl ester**
 3-oxo-2-pentyl-cyclopentane-acetic acid methyl ester**
 1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-ethanone*

5	3-methyl-5-propyl-cyclohex-2-en-1-one*
	4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-one**
	4-(2,6,6-trimethylcyclohex-2-en-1-yl)butan-2-one**
	2-methyl-5-(1-methylethenyl)-cyclohex-2-en-1-one*
	cyclopentadecanone**
	1-(4-hydroxyphenyl)-butan-3-one**
	4-benzo-1,3-dioxo-5-yl-but-2-one**
	4-(1,3-benzodioxol-5-yl)-2-butanone**
10	nonan-3-one*
	nonan-2-one*
	octan-2-one*
	2-heptanone*
	butan-2-one*
	6-methyl-hept-5-en-2-one*
15	6,10-dimethyl-undeca-5,9-dien-2-one*
	1-(2,4,4-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one*
	1-(2-cyclohexen)-2,4,4-trimethyl-but-2-enone*
	carvone**
	2-hexyl-cyclo-pent-2-en-1-one**
20	2-pentyl-cyclopent-2-en-1-one
	3-methyl-2-pentyl-cyclopent-2-en-1-one**
	2-hexylidenecyclopentanone*
	3,5-diethyl-5,6-dimethyl-2-cyclohexenone*
	4,4A,5,6,7,8-hexahydro-6-isopropenyl-4,4A-dimethyl-2 (3H)-naphthalenone**
25	3-methyl-6-propylidenecyclohexanone*
	4-(1-methylethyl)-cyclohex-2-en-1-one
	(E)-oct-3-en-2-one
	1-(2,3,4,7,8, 8A-hexahydro-3,6,8,8-tetramethyl-1H-3A,7-methanoazulen-5-yl)-ethanone*
	2-hydroxy-3,5-dimethyl-cyclopent-2-ene-1-one*
30	1-(3,3-dimethyl-1-cyclohexen-1-yl)ethanone*
	1-(2,4,6-trimethylcyclohex-3-en-1-yl)-but-1-en-3-one acetylisolongifolene
	2-(3-methylbut-2-en-1-yl)-3-methyl-cyclopent-2-en-1-one
	2,6,6-trimethyl-1,3-cyclohexadienyl-1-carbaldehyde**
	3-methyl-5-(2,2,3-trimethylcyclopent-3-ene-1-yl)pent-3-ene-2-one*
35	5-butylidene-2,2,4-trimethylcyclopentanone
	1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4one**
	3-methyl-5-propyl-cyclohex-2-en-1-one**
	4,4A,5,6,7,8-hexahydro-6-isopropyl-2 (3H)-naphthalenone
	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-butan-2-one**
40	4-methoxyphenylethanone**
	acetophenone*
	1-(2-naphthalenyl)-ethanone**
	3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one**
	2-acetylpyrazine*
45	3,5,5-trimethyl-cyclohex-2-en-1,4-dione*
	(E)-5-methyl-2-hepten-4-one
	acetyl diisoamylene**
	dec-3-en-2-one
	2-ethyl-3, 6, 6-trimethylcyclohex-2-enyl-but-2-en-1-one
50	1-(5,5-dimethyl-1(6)-cyclohexen-1-yl)-4-penten-1-one**
	1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-but-2-ene-1-one**
	1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-but-2-ene-1-one**
	1-(2,6, 6,trimethyl-3-cyclohexen-1-yl)-but-2-ene-1-one**
	2,4,4,5,5-pentamethyl-1-cyclopentene-1-yl-ethanone*
55	

whereby * indicates the preferred ketones and ** indicate the more preferred ketones.

[0026] Examples of alcohols are primary, secondary and tertiary alcohols and phenols such as:

	amyl alcohol
	hexyl alcohol*
	2-hexyl alcohol*
	heptyl alcohol*
5	octyl alcohol*
	nonyl alcohol*
	decyl alcohol*
	undecyl alcohol*
	lauryl alcohol*
10	myristic alcohol
	3-methyl-but-2-en-1-ol*
	3-methyl-1-pentanol
	cis-3-hexenol*
	cis-4-hexenol*
15	3,5,5-trimethyl-hexanol
	3,4,5,6,6-pentamethylheptan-2-ol*
	citronellol*
	geraniol*
	oct-1-en-3-ol
20	2,5,7-trimethyl-octan-3-ol
	2-cis-3,7-dimethyl-2,6-octadien-1-ol
	6-ethyl-3-methyl-5-octen-1-ol*
	3,7-dimethyl-oct-3,6-dienol*
	3,7-dimethyloctanol*
25	7-methoxy-3,7-dimethyl-octan-2-ol*
	cis-6-nonenoil*
	5-ethyl-2-nonanol
	6,8-dimethyl-2-nonanol*
	2,2,8-trimethyl-7(8)-nonene-3-ol
30	nona-2, 6-dien-1-ol
	4-methyl-3-decen-5-ol*
	dec-9-en-1-ol
	benzylalcohol
	2-methyl-undecanol
35	10-undecen-1-ol
	1-phenyl-ethanol*
	2-phenyl-ethanol*
	2-methyl-3-phenyl-3-propenol
	2-phenyl-propanol*
40	3-phenyl-propanol*
	4-phenyl-2-butanol
	2-methyl-5-phenyl-pentanol*
	2-methyl-4-phenyl-pentanol*
	3-methyl-5-phenyl-pentanol*
45	2-(2-methylphenyl)-ethanol*
	4-(1-methylethyl)-benzene-methanol
	4-(4-hydroxyphenyl) -butan-2-one*
	2-phenoxy-ethanol*
	4-(1-methylethyl)-2-hydroxy-1-methyl benzene
50	2-methoxy-4-methyl-phenol
	4-methyl-phenol
	anisic alcohol*
	p-tolyl alcohol*
	cinnamic alcohol*
55	vanillin*
	ethyl vanillin*
	eugenol*
	isoeugenol*

thymol
 anethol*
 decahydro-2-naphthalenol
 borneol*
 5 cedrenol*
 farnesol*
 fenchyl alcohol*
 menthol*
 10 3,7,11-trimethyl-2,6,10-dodecatrien-1-ol
 alpha ionol*
 tetrahydro ionol*
 15 2-(1,1-dimethylethyl)cyclohexanol*
 3-(1,1-dimethylethyl)cyclohexanol*
 4-(1,1-dimethylethyl)cyclohexanol*
 15 4-isopropyl-cyclohexanol
 6,6-dimethyl-bicyclo[3.3.1]hept-2-ene-2-ethanol
 6,6-dimethyl-bicyclo[3.1.1]hept-2-ene-methanol*
 p-menth-8-en-3-ol*
 20 3,3,5-trimethyl-cyclohexanol
 2,4,6-trimethyl-3-cyclohexenyl-methanol*
 4-(1-methylethyl)-cyclohexyl-methanol*
 4-(1,1-dimethylethyl)-cyclohexanol
 2-(1,1-dimethylethyl)-cyclohexanol
 2,2,6-trimethyl-alpha-propyl-cyclohexane propanol*
 25 5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol*
 3-methyl-5-(2,2,3-trimethylcyclopentyl-3-enyl)pent-4-en-2-ol*
 2-ethyl-4(2,2,3-trimethylcyclopentyl-3-enyl)but-2-en-1-ol*
 4-(5,5,6-trimethylbicyclo[2.2.1]hept-2-yl)-cyclohexanol*
 2-(2-methylpropyl)-4-hydroxy-4-methyl-tetrahydropyran*
 30 2-cyclohexyl-propanol*
 2-(1,1-dimethylethyl)-4-methyl-cyclohexanol*
 1-(2-tert-butyl-cyclohexyloxy)-2-butanol*
 1-(4-isopropyl-cyclohexyl)-ethanol*
 1-(4-hydroxyphenyl)-butan-3-one
 35 2,6-dimethyl-oct-7-en-2-ol**
 2,6-dimethyl-heptan-2-ol**
 3,7-dimethyl-octa-1,6-dien-3-ol**

* indicates preferred alcohols and ** indicate the more preferred alcohols.

40 [0027] Examples of lactones include:

6-methyl-pyran-2-one
 5-heptyldihydro-2(3H)-furanone*
 5-pentyldihydro-2(3H)-furanone*
 45 5-(3-hexenyl)-dihydro-5-methyl-(Z)-2 (3H)-furanone
 5-hexyldihydro-5-methyl-2(3H)-furanone
 5-hexyldihydro-2(3H)-furanone*
 5-octyldihydro-2 (3H)-furanone
 8-(1-methylethyl)-1-oxaspiro[4.5]-decan-2-one*
 50 8-methyl-1-oxaspiro[4.5]decan-2-one
 8-ethyl-1-oxaspiro[4.5]decan-2-one
 5-(1,5-dimethyl-4-hexenyl)-dihydro-2(3H)-furanone
 2-oxo-5-butyl-tetrahydrofuran*
 55 4-methyl-5-pentyl-dihydro-2(3H)-furan-2-one
 5-hexyldihydro-5-methyl-2(3H)-furanone
 dihydro-5-methyl-5-vinyl-2(3H)-furanone
 octahydro-2H-1-benzopyran-2-one
 tetrahydro-6-pentyl-2H-pyran-2-one

5 tetrahydro-6-hexyl-2H-pyran-2-one
 tetrahydro-6-heptyl-2H-pyran-2-one
 tetrahydro-6-(3-pentenyl)-(E)-2H-pyran-2-one
 tetrahydro-6-(2-pentenyl)-(Z)-2H-pyran-2-one
 (E)-oxacycloheptadec-10-en-one**
 oxacyclohexadecan-2-one**
 dodeca-12-olide

whereby * indicates the preferred lactones.

10 [0028] It is a matter of course, that it is not possible to give a complete list of the organoleptic especially odoriferous and/or antimicrobial aldehydes, ketones, alcohols and lactones which are generated as a result of the desired cleavage of the esters of formula I by skin bacteria, by enzymes, by elevated temperatures, by acidic and/or alkaline pH-values or by light. The skilled person is, however, quite aware of those aldehydes, ketones, alcohols and lactones which provide the desired organoleptic, e.g. fragrance and odour masking and/or antimicrobial effects.

15 [0029] While manufacturing compositions, the precursors of the invention may be used according to methods known to the perfumer, such as e.g. from W.A. Poucher, Perfumes, Cosmetics, Soaps, 2, 7th Edition, Chapman and Hall, London 1974.

20 [0030] The compounds of formula I may preferably be used as sustained release odorants but also to mask or attenuate undesirable odours or to provide additional odours not initially present in consumer products, i.e. personal care products such as cosmetic products destined for application to human skin such as underarm deodorants or antiperspirants or other deodorants contacting the body, or in hand lotions, baby powders, baby lotions, ointments, foot products, facial cleansers, body wipes, facial make-up, colognes, after-shave lotions, shaving creams, etc. Additional applications include laundry detergents, fabric softeners, fabric softener sheets, (automatic) dishwasher detergents, and other enzyme-containing consumer products. Further applications are air fresheners and odorants, odour masking agents and/or antimicrobial agents.

25 [0031] The amount required to produce the desired, overall effect varies depending upon the particular compounds of formula I chosen, the product in which it will be used, and the particular effect desired.

30 [0032] For example, depending upon the selection and concentration of the compound chosen, when a compound of the formula I is added either singly or as a mixture, e.g. to a deodorant or laundry product composition at levels ranging from about 0.1 to about 10 % by weight, or most preferred about 0.25 to about 4 % by weight, an odorant, i.e. an odoriferous, aldehyde, ketone, alcohol or lactone in an "organoleptically effective amount" is released when the product is used. This newly formed odorant serves to enhance the odour of the product itself or of a fragrance present in the product.

35 [0033] Compounds of formula I can be prepared by using a wide variety of methods known to the skilled chemist.

For example, for the synthesis of esters see Comprehensive Organic Chemistry, vol 2, D. Barton, W.D. Ollis, Pergamon Press, p. 871.

For example, for the synthesis of carbonates see Comprehensive Organic Chemistry, vol 2, D. Barton, W.D. Ollis, Pergamon Press, p. 1070.

40 For example, for the synthesis of carbamates see Comprehensive Organic Chemistry, vol 2, D. Barton, W.D. Ollis, Pergamon Press, p. 1083.

Convenient methods are outlined in the Examples without limiting the invention thereto.

Example 1

Acetic acid 3-(4-tert-butyl-phenyl)-2-methyl-propenyl ester

45 [0034] A solution of 200 g 2-methyl-3-(4-*tert*-butylphenyl)-propanal, 280 ml triethylamine and 13.4 g sodium acetate in 800 ml of acetic anhydride was stirred at 120°C for 5.5 hours. Then the solution was cooled, water was added and the water phase was extracted with hexane. The organic phase was washed with 2N NaOH and water to neutrality, dried and evaporated to dryness. The residue was distilled to yield 185 g of a colourless liquid.

50 NMR (CDCl₃):

δ 7.35-6.97 (m, 5H), 3.43+3.21 (s, 2H, E/Z), 2.13 (s, 3H), 1.60 (s, 3H), 1.30 (s, 9H) ppm.

Example 2

Acetic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester

55 [0035] According to the procedure of example 1, acetic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester was prepared

from 3-(3-isopropylphenyl)-butanal, acetic anhydride, sodium acetate and triethylamine.

Example 3

5 4-Oxo-undecanoyl chloride

[0036] To a suspension of 50 g 4-oxo-undecanoic acid (Synthesis, 1987, 408) in 350 ml of ether, 22.15 g pyridine was dropped in at 0°C. Then a solution of 32.72 g thionyl chloride in 50 ml of ether was dropped in at 0-5°C and then the reaction mixture was stirred for 20 hours at room temperature. Then the reaction mixture was filtered and evaporated to dryness. The residue (53.83 g yellow oil) was not further purified.

Example 4

15 4-Oxo-decanoic acid 3,7-dimethyl-oct-6-enyl ester

[0037] A solution of 20.0 g 4-oxo-1-decanoic acid (Synthesis, 1987, 408), 16.8 g citronellol extra and 0.5 g p-toluenesulfonic acid in 150 ml of cyclohexane was refluxed in a flask equipped with a Dean-Stark trap for 3 hours. Then the reaction mixture was cooled, diluted with ether, washed with saturated NaHCO_3 and water. The organic phase was dried, filtered and evaporated to dryness. The resulting oil was purified by chromatography to yield 31.7 g of a yellow oil.

20 NMR (CDCl_3):

δ 5.04-5.19 (m, 1H), 4.11-4.17 (m, 2H), 2.68-2.79 (m, 2H), 2.53-2.60 (m, 2H), 2.41-2.48 (t, 2H), 2.03-1.91 (q, 2H), 1.75-1.44 (m, 6H), 1.43-1.08 (m, 12H), 0.92-0.84 (m, 6H) ppm.

Example 5

25 4-Oxo-decanoic acid hex-3-enyl ester

[0038] According to the procedure of Example 4, 4-oxo-decanoic acid hex-3-enyl ester was prepared from 4-oxo-decanoic acid, cis-3-hexenol and p-toluenesulfonic acid.

30 Example 6

4-Oxo-undecanoic acid hex-3-enyl ester

35 [0039] According to the procedure of Example 4, 4-oxo-undecanoic acid hex-3-enyl ester was prepared from 4-oxo-undecanoic acid, cis-3-hexenol and p-toluenesulfonic acid.

Example 7

40 4-Oxo-nonanoic acid hex-3-enyl ester

[0040] According to the procedure of Example 4, 4-oxo-nonanoic acid hex-3-enyl ester was prepared from 4-oxo-nonanoic acid (Synthesis, 1987, 408), cis-3-hexenol and p-toluenesulfonic acid.

45 Example 8

4-Oxo-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

[0041] A solution of 20 g 4-oxo-nonanoic acid, 19.3 g geraniol, 26.8 g N,N-dicyclohexyl-carbodiimide and 1.0 g 4-pyrrolidinopyridine in 300 ml of dichloromethane was stirred for 24 hours at room temperature. The precipitate was filtered off, the filtrate was diluted with ether, washed with aqueous hydrochloric acid, saturated NaHCO_3 and brine. The organic phase was dried, filtered and evaporated to dryness. The resulting oil-crystal mixture was purified by chromatography to yield 21.4 g of a colourless oil.

NMR (CDCl_3):

55 δ 5.32 (t, 1H), 5.09 (m, 1H), 4.10 (d, 2H), 2.71 (m, 2H), 2.52 (m, 2H), 2.43 (t, 2H), 2.07 (m, 4H), 1.77-1.50 (m, 11H), 1.29 (m, 4H), 0.91 (t, 3H) ppm.

Example 94-Oxo-decanoic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester

5 [0042] According to the procedure of example 8, 4-oxo-decanoic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester was prepared from 4-oxo-decanoic acid and (\pm)-linalool.

Example 104-Oxo-decanoic acid 1,1,5-trimethyl-hexyl ester

10 [0043] According to the procedure of example 8, 4-oxo-decanoic acid 1,1,5-trimethyl-hexyl ester was prepared from 4-oxo-decanoic acid and 2,6-dimethyl-heptan-2-ol.

Example 114-Oxo-undecanoic acid 2-benzyloxycarbon 1-2-benzyloxy carbonylamino-ethyl ester

15 [0044] According to the procedure of Example 8, 4-oxo-undecanoic acid 2-benzyloxycarbonyl-2-benzyloxy carbonylamino-ethyl ester was prepared from 4-oxo-undecanoic acid, 2-benzyloxycarbonylamino-3-hydroxy propionic acid benzyl ester, N,N'-dicyclohexyl-carbodiimide and dimethylaminopyridine.

Example 124-Oxo-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methylpropenyl ester

20 [0045] To a solution of 43.79 g acetic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester in 200 ml of tetrahydrofuran, a solution of 27.16 g potassium *tert*-butoxide in 200 ml of tetrahydrofuran was dropped in at -78°C. After stirring at this temperature for 90 minutes, a solution of 53.00 g 4-oxo-undecanoyl chloride in 200 ml of tetrahydrofuran was dropped in. After stirring at -78°C for 2.5 hours, the solution was quenched with saturated sodium bicarbonate solution and diluted with ether. The organic phase was washed with saturated sodium bicarbonate solution and brine, dried and evaporated to dryness. The residue was purified by thin-film distillation and chromatography to yield 25.73 g of a yellow oil.

NMR (CDCl₃):

25 δ 7.37-6.93 (m, 5H), 3.42+3.22 (s, 2H, E/Z), 2.82-2.61 (m, 4H), 2.52-2.38 (m, 2H), 1.70-1.48 (m, 5H), 1.47-1.15 (m, 17H), 0.98-0.80 (t, 3H) ppm.

Example 134-Oxo-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester

30 [0046] According to the procedure of example 12, 4-oxo-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester was prepared from acetic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester, 4-oxo-undecanoyl chloride and potassium *tert*-butoxide.

Example 144-Hydroxy-decanoic acid 3,7-dimethyl-oct-6-enyl ester

35 [0047] A solution of 2.0 g sodium borohydride in 30 ml of water was cooled to 5°C. A solution of 4-oxo-decanoic acid 3,7-dimethyl-oct-6-enyl ester in 75 ml of THF was added to the reaction during 12 minutes and the resulting reaction mixture was stirred at room temperature for 5 hours. Then the reaction mixture was diluted with ether, washed with saturated NaHCO₃, brine and water. The organic phase was dried, filtered and evaporated to dryness. The resulting liquid was purified by chromatography to yield 7.6 g of a liquid.

50 NMR (CDCl₃):

55 δ 5.09 (bt, 1H), 4.11 (t, 2H), 3.61 (m, 1H), 2.42 (t, 2H), 2.07 (m, 2H), 2.12-1.02 (m, 22H), 0.88 (m, 6H) ppm.

Example 154-Hydroxy-nonanoic acid hex-3-enyl ester

5 [0048] According to the procedure of Example 14, 4-hydroxy-nonanoic acid hex-3-enyl ester was prepared from 4-oxononanoic acid hex-3-enyl ester, sodium borohydride and water.

Example 164-Hydroxy-decanoic acid hex-3-enyl ester

[0049] According to the procedure of Example 14, 4-hydroxydecanoic acid hex-3-enyl ester was prepared from 4-oxodecanoic acid hex-3-enyl ester, sodium borohydride and water.

Example 174-Hydroxy-decanoic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester

20 [0050] According to the procedure of Example 14, 4-hydroxy-decanoic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester was prepared from 4-oxo-decanoic acid 1,5-dimethyl-1-vinylhex-4-enyl ester, sodium borohydride and water.

Example 184-Hydroxy-undecanoic acid hex-3-enyl ester

25 [0051] According to the procedure of Example 14, 4-hydroxy-undecanoic acid hex-3-enyl ester was prepared from 4-oxo-undecanoic acid hex-3-enyl ester, sodium borohydride and water.

Example 194-Hydroxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

30 [0052] According to the procedure of Example 14, 4-hydroxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester was prepared from 4-oxo-nonanoic acid 3,7-dimethyl-octa-2,6dienyl ester, sodium borohydride and water.

Example 204-Hydroxy-decanoic acid 1,1,5-trimethyl-hexyl ester

40 [0053] According to the procedure of Example 14, 4-hydroxydecanoic acid 1,1,5-trimethyl-hexyl ester was prepared from 4-oxo-decanoic acid 1,1,5-trimethyl-hexyl ester, sodium borohydride and water.

Example 214-Hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester4-Hydroxy-undecanoic acid sodium salt

50 [0054] To a solution of 43.6 g sodium hydroxide in 150 ml of methanol heated to reflux, 200 g gamma-undecalactone were dropped in. After stirring for 2 hours at reflux, the mixture was cooled to room temperature and evaporated to dryness. The resulting crystals were washed with hexane to yield 240 g colourless crystals.

NMR (CDCl_3):

δ 5.1-4.8 (br s, OH), 3.63-3.42 (m, 1H), 2.39-2.20 (t, 2H), 1.89-1.52(m, 2H), 1.51-1.15 (m, 12H), 1.00-0.81 (t, 3H) ppm.

55 1-Chloro-3,7-dimethyl-octa-2,6-diene

[0055] To a mixture of 170 g linalool and 20 mg bismuth(III)-oxide heated to 60 °C, 130.5 g trimethylchlorosilane were dropped in. Then the mixture was cooled to room temperature and the organic layer was separated. The resulting

oil was purified by distillation to yield 158.35 g of a colourless oil.

NMR (CDCl₃):

δ 5.56-5.35 (t, 1H), 5.18-4.99 (m, 1H), 4.16-4.02 (d, 2H), 2.26-1.91 (m, 4H), 1.89-1.45 (m, 9H) ppm.

5 4-Hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

[0056] A mixture of 155 g 1- chloro-3,7-dimethyl-octa-2,6-diene, 202 g 4-hydroxy-undecanoic acid sodium salt and 5 g tetrabutylammoniumbromide in 800 ml of dimethylformamide was heated to 50°C. After stirring for 24 hours, the mixture was cooled to room temperature and filtered through Celite. The filtrate was diluted with ether, washed with water, 2N HCl, saturated sodium bicarbonate and brine. The organic phase was dried and evaporated to dryness. The resulting yellow oil was purified by wipe film distillation to yield 96.6 g of a yellow oil.

10 NMR (CDCl₃):

δ 5.42-5.37 (t, 1H), 5.16-5.01 (m, 1H), 4.65-4.53 (m, 2H), 3.69-3.52 (m, 1H), 2.60-2.22 (m, 2H), 2.20-1.95 (m, 4H), 1.89-1.12 (m, 24H), 1.02-0.78 (t, 3H) ppm.

15

Example 22

4-Hydroxy-undecanoic acid dodecylamide

20 [0057] A solution of 19.0 g aluminium chloride, dissolved in methylene chloride, was cooled to 0°C and 46.5 g dodecylamine in methylene chloride was added dropwise (exothermic). At room temperature 19.3 g gamma-undecalactone was added rapidly. The temperature rose to 36°C. The reaction was stirred at room temperature for 4 hours. The mixture was quenched with water and filtered over Celite. The liquid was extracted with ether and washed with water and brine. The solution was dried, filtered and evaporated to dryness. The resulting brown crystals were purified by recrystallisation from ether/ethylacetate to give pale yellow crystals.

25 NMR (CDCl₃):

δ 5.7-5.6 (s, 1H), 3.7-3.55 (m, 1H), 3.3-3.15 (m, 2H), 2.4-2.3 (m, 2H), 1.95-1.2 (m, 34H), 0.95-0.85 (m, 6H) ppm.

30 Example 23

4-Hydroxy-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester

[0058] A solution of 10.00 g 4-oxo-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester was dissolved in 60 ml methanol and a trace of bromocresol green was added. When 1.63 g sodium cyanoborohydride was added, the colour changed immediately from yellow to deep blue. Several drops of 2N HCl/methanol solution turned the colour of the reaction back to yellow. The reaction was stirred for 2 1/2 hours, with occasional addition of acid to maintain the yellow colour. The reaction mixture was evaporated to dryness and water was added to the residue. This solution was extracted with ether and washed with water. The solution was dried, filtered and evaporated to dryness to yield 10.07 g of a colourless oil.

40 NMR (CDCl₃):

δ 7.35-7.25 (m, 2H), 7.15-7.03 (m, 3H), 3.72-3.57 (m, 1H), 3.27 + 3.2 (s, 2H, E/Z), 2.62-2.5 (m, 4H), 2.5-2.4 (m, 2H), 1.65-1.56 (m, 5H), 1.35-1.21 (m, 17H), 0.95-0.82 (m, 3H) ppm.

45 Example 24

4-Hydroxy-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester

[0059] According to the procedure of Example 23, 4-hydroxy-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester was prepared from 4-oxo-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester and sodium cyanoborohydride.

50 Example 25

4-Hydroxy-undecanoic acid 2-benzyloxycarbonyl-2-benzyloxy carbonylamino-ethyl ester

55 [0060] According to the procedure of Example 23, 4-hydroxy-undecanoic acid 2-benzyloxycarbonyl-2-benzyloxy carbonylamino-ethyl ester was prepared from 4-oxo-undecanoic acid 2-benzyloxycarbonyl-2-benzyloxy carbonylamino-ethyl ester and sodium cyanoborohydride.

Example 263-[2-(*tert*-Butyl-dimethyl-silanyloxy)- phenyl]-acryloyl chloride5 3-[2-(*tert*-Butyl-dimethyl-silanyloxy)- phenyl]-acrylic acid *tert*-butyl-dimethyl-silanyl ester

[0061] To a solution of 10.00 g 3-(2-hydroxy-phenyl)-acrylic acid (Tiemann; Herzfeld, Chem. Ber., 10 (1877), 285) and 19.3 g *tert*-butyldimethylsilyl chloride in 40 ml of dimethylformamide was added 16.59 g imidazole. After stirring at 60°C for 6 hours, the mixture was poured onto water and extracted with hexane. The organic phase was washed with saturated sodium bicarbonate solution and water, dried and evaporated to dryness. The residue was not further purified.

3-[2-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-acryloyl chloride

15 [0062] To a solution of 10.01 g 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid *tert*-butyl-dimethyl-silanyl ester in 25 ml of dichloromethane, three drops of dimethylformamide were added and 4.14 g oxalyl chloride was dropped in at 0°C. After stirring at 0°C for 90 minutes and at room temperature overnight, the mixture was evaporated to dryness. The resulting brown solid (7.52 g) was not further purified.

NMR (CDCl₃):

20 δ 8.09-7.96 (d, 1H), 7.33-7.25 (d, 1H), 7.15-6.98 (m, 1H), 6.80-6.56 (m, 2H), 6.42-6.30 (d, 1H), 0.80 (s, 9H), 0.01 (s, 6H) ppm.

Example 2725 Tetradecanoic acid 1-(2-hex-3-enyloxycarbonyl-ethyl)-heptyl ester

[0063] To a mixture of 1.10 g of 4-hydroxy-decanoic acid hex-3-enyl ester, 0.64 g pyridine and 0.1 g dimethylaminopyridine in 5 ml tetrahydrofuran was slowly added a solution of 1.10 g myristoyl chloride in 5 ml tetrahydrofuran. The mixture was stirred for 16 hours at room temperature.

30 Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water, dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silica gel to give 1.81 g of a colourless liquid.

NMR (CDCl₃):

35 δ 5.56 (m, 1H), 5.37 (m, 1H), 4.89 (q, 1H), 4.06 (t, 2H), 2.38-2.19 (m, 6H), 2.05 (q, 2H), 1.84 (m, 2H), 1.71-1.13 (m, 4H), 1.25 (s, 28H), 0.97 (t, 3H), 0.93-0.84 (m, 6H) ppm.

Example 28Tetradecanoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxy carbonyl)-ethyl]-octyl ester

40

[0064]

[0065] According to the procedure of Example 27, tetradecanoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxy carbonyl)-ethyl]-octyl ester was prepared from 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine, dimethylaminopyridine and myristoyl chloride.

45

Example 29Benzoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxy carbonyl)-ethyl]-octyl ester

50

[0066] According to the procedure of Example 27, benzoic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxy carbonyl)-ethyl]-octyl ester was prepared from 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine, dimethylaminopyridine and benzoyl chloride.

Example 30

55

Dodecanoic acid 1-[2-(3,7-dimethyl-oct-6-enyloxycarbonyl)-ethyl]-heptyl ester

[0067] According to the procedure of Example 27, dodecanoic acid 1-[2-(3,7-dimethyl-oct-6-enyloxycarbonyl)-ethyl]-

heptyl ester was prepared from 4-hydroxy-decanoic acid 3,7-dimethyl-oct-6-enyl ester, pyridine, dimethylaminopyridine and lauroyl chloride.

5 Example 31

Dodecanoic acid 1-(2-[3-(4-tert-butyl-phenyl)-2-methylpropenoxy carbonyl]-ethyl)octyl ester

[0068] According to the procedure of Example 27, dodecanoic acid 1-[2-[3-(4-tert-butyl-phenyl)-2-methyl-propenoxy carbonyl]-ethyl]octyl ester was prepared from 4-hydroxy-undecanoic acid 3-(4-tert-butyl-phenyl)-2-methyl-propenoxy ester, lauroyl chloride, pyridine and dimethylaminopyridine.

10 Example 32

Dodecanoic acid 1-[2-[3-(3-isopropyl-phenyl)-but-1-enyloxy carbonyl]-ethyl] octyl ester

[0069] According to the procedure of Example 27, dodecanoic acid 1-[2-[3-(3-isopropyl-phenyl)-but-1-enyloxy carbonyl]-ethyl]octyl ester was prepared from 4-hydroxy-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester, lauroyl chloride, pyridine and dimethylaminopyridine.

15 Example 33

Dodecanoic acid 1-[2-(2-benzyloxy carbonyl-2-benzyloxy carbonyl amino-ethoxycarbonyl)-ethyl]octyl ester

[0070] According to the procedure of Example 27, dodecanoic acid 1-[2-(2-benzyloxy carbonyl-2-benzyloxy carbonyl amino-ethoxycarbonyl)-ethyl]octyl ester was prepared from 4-hydroxy-undecanoic acid 2-benzyloxy carbonyl-2-benzyloxy carbonyl amino-ethyl ester, lauroyl chloride and pyridine.

20 Example 34

30 4-Phenethyloxy carbonyloxy-decanoic acid 3,7-dimethyl-oct-6-enyl-ester

[0071] To a mixture of 3 g 4-hydroxy-decanoic acid 3,7-dimethyloct-6-enyl ester and 1.45 g pyridine in 7 ml tetrahydrofuran was slowly added a solution of 1.87 g chlorocarbonic acid phenethyl ester (Schiving et al., Bull. Soc. Chim. Fr. (4), 43, 1928, 858) in 7 ml tetrahydrofuran. The mixture was stirred for 16 hours. Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water, dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silica gel to give 3.91 g of a colourless liquid.

NMR (CDCl_3):

35 δ 7.35-7.18 (m, 5H), 5.08 (m, 1H), 4.70 (m, 1H), 4.34 (t, 2H), 4.10 (t, 2H), 2.98 (t, 2H), 2.34 (m, 2H), 2.04-1.74 (m, 4H), 1.72-1.08 (m, 20H), 0.96-0.84 (m, 7H) ppm.

40 Example 35

45 4-Phenethyloxy carbonyloxy-decanoic acid hex-3-enyl ester

[0072] According to the procedure of Example 34, 4-phenethyloxy carbonyloxy-decanoic acid hex-3-enyl ester was prepared from 4-hydroxy-decanoic acid hex-3-enyl ester, pyridine and chlorocarbonic acid phenethyl ester (Schiving et al., Bull. Soc. Chim. Fr. (4), 43, 1928, 858).

50 Example 36

4-Hex-3-enyloxy carbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

55 [0073] According to the procedure of Example 34, 4-hex-3-enyloxy carbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester was prepared from 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine and chlorocarbonic acid hex-3-enyl ester (K. F. Podraza, J. Heterocycl. Chem. 1984, 21(4), 1197).

Example 374-Ethoxycarbonyloxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

5 [0074] According to the procedure of Example 34, 4-ethoxycarbonyloxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester was prepared from 4-hydroxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine and chlorocarbonic acid ethyl ester (commercially available).

Example 384-Phenethyloxycarbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

10 [0075] According to the procedure of Example 34, 4-phenethyloxycarbonyloxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester was prepared from 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine and chlorocarbonic acid phenethyl ester (Schiving et al., Bull. Soc. Chim. Fr. (4), 43, 1928, 858).

Example 394-Hex-3Z-enyloxycarbonyloxy-undecanoic acid 3-(4-isopropyl-phenyl-but-1-enyl ester

15 [0076] According to the procedure of Example 34, 4-hex-3Z-enyloxycarbonyloxy-undecanoic acid 3-(4-isopropyl-phenyl)-but-1-enyl ester was prepared from 4-hydroxy-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester, cis-hexenol-chloroformate and pyridine.

Example 404-(3-Methyl-5-phenyl-pentyloxycarbonyloxy)-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester

20 [0077] According to the procedure of Example 34, 4-(3-methyl-5-phenyl-pentyloxycarbonyloxy)-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester was prepared from 4-hydroxy-undecanoic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester, 3-methyl-5-phenyl-pentanol-chloroformate and pyridine.

Example 413-[2-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid 1-(2-hex-3-enyloxycarbonyl-ethyl)-hexyl ester

25 [0078] According to the procedure of Example 34, 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid 1-(2-hex-3-enyloxycarbonyl-ethyl)-hexyl ester was prepared from 4-hydroxy-nonanoic acid hex-3-enyl ester, 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-acryloyl chloride and pyridine.

Example 424-(4-Allyl-2-methoxy-phenoxy carbonyloxy)-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester

30 [0079] According to the procedure of Example 34, 4-(4-allyl-2-methoxy-phenoxy carbonyloxy)-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester was prepared from 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, pyridine and chlorocarbonic acid-(4-allyl-2-methoxyphenyl) ester (Einhorn, D.R.P. 224108).

Example 434-(Bis-decyl-carbamoyloxy)-undecanoic acid hex-3-enyl ester

35 [0080] To 6.20 ml of an ice-cooled 20% solution of phosgene in toluene was slowly added a solution of 3 g 4-hydroxy-undecanoic acid hex-3-enyl ester and 0.93 g pyridine in 3 ml toluene. The reaction mixture was stirred for 16 hours at room temperature. A mixture of 3.48 g didecylamine and 0.93 g pyridine was added and the mixture was stirred for another 16 hours.

40 [0081] Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water, dried over magnesium sulfate and evaporated to dryness. The residue

was chromatographed on silica gel to give 2.9 g of a colourless liquid.

NMR (CDCl₃):

δ 5.0 (m, 1H), 5.32 (m, 1H), 5.28 (quint, 1H), 4.06 (t, 2H), 3.18 (m, 4H), 2.35 (m, 4H), 2.05 (quint, 2H), 2.37 (m, 2H), 1.67-1.41 (m, 10H), 1.28 (bs, 30H), 0.98 (t, 3H), 0.88 (m, 9H) ppm.

5

Example 44

Succinic acid bis-[1-[2-(3,7-dimethyl-octa-2,6 dienyloxycarbonyl)-ethyl]-octyl] ester

[0082] To an ice cooled solution of 0.91 g succinic acid dichloride in 15 ml tetrahydrofuran was slowly added a mixture of 4 g 4-hydroxy-undecanoic acid 3,7-dimethyl-octa-2,6-dienyl ester and 0.93 g pyridine in 15 ml tetrahydrofuran. The mixture was stirred for 16 hours at room temperature.

Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water, dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silica gel to give 2.2 g of a colourless liquid.

NMR (CDCl₃):

δ 5.33 (bt, 2H), 5.09 (m, 2H), 4.91 (quint, 2H), 4.6 (m, 4H), 2.60 (m, 5H), 2.33 (m, 4H), 2.09 (m, 8H), 1.8 (m, 4H), 1.71 (bs, 12H), 1.62 (s, 6H), 1.52 (m, 4H), 1.27 (bs, 20H), 0.91 (bt, 6H) ppm.

20 Example 45

Succinic acid 1-[2-(1,5-dimethyl-1-vinyl-hex-4-enyloxycarbonyl)-ethyl]-heptyl ester hex-3-enyl ester

Succinic acid monohex-3-enyl ester

25

[0083] A mixture of 100 g succinic anhydride, 100 g cis-3-hexen-1-ol, 88.5 ml pyridine and 7.3 g dimethylaminopyridine in 500 ml dichloromethane was refluxed for 4 hours. Ether was added and the mixture was acidified with HCl 2N then washed with brine. The organic layer was dried over magnesium sulfate and concentrated. The residue was distilled under vacuum to afford 185 g of product.

NMR (CDCl₃):

δ 11.1 (bs, 1H), 5.53 (m, 1H), 5.31 (m, 1H), 4.11 (t, 2H), 2.64 (m, 4H), 2.39 (q, 2H), 2.07 (quint, 2H), 0.97 (t, 3H) ppm.

2-chlorocarbonic-propionic acid hex-3-enyl ester

[0084] To an ice cooled mixture of 184 g of succinic acid monohex-3-enyl ester and 79 g pyridine in 750 ml diethylether was added a solution of 69 ml thionyl chloride in 150 ml diethylether. The mixture was stirred for 17 hours at room temperature then filtered and concentrated to afford 184 g of a brown oil.

NMR (CDCl₃):

δ 5.02 (m, 1H), 4.82 (m, 1H), 4.12 (dt, 2H), 3.21 (t, 1H), 2.72 (m, 5H), 2.39 (q, 2H), 2.04 (quint, 2H), 0.98 (t, 3H) ppm.

40

Succinic acid 1-[2-(1,5-dimethyl-1-vinyl-hex-4-enyloxycarbonyl)-ethyl]-heptyl ester hex-3-enyl ester

[0085] To a mixture of 3 g 4-hydroxy-decanoic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester and 1.6 g pyridine in 15 ml tetrahydrofuran was added a solution of 2.2 g 2-chlorocarbonic-propionic acid hex-3-enyl ester in 15 ml tetrahydrofuran.

45 The mixture was stirred for 16 hours at room temperature.

Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water, dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silica gel to give 1.9 g of a colourless liquid.

NMR (CDCl₃): δ 5.96 (dd, 1H), 5.52 (m, 1H), 5.34 (m, 1H), 5.21-5.03 (m, 2H), 4.08 (t, 2H), 2.62 (s, 4H), 2.48-2.21 (m, 4H), 2.15-1.71 (m, 8H), 1.70 (s, 3H), 1.54-1.46 (m, 8H), 1.23 (bs, 8H), 0.96 (t, 3H), 0.88 (bt, 3H) ppm.

50 Example 46

Succinic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxycarbonyl)-ethyl]-hexyl ester hex-3Z-enyl ester

55

[0086] According to the procedure of Example 45, succinic acid 1-[2-(3,7-dimethyl-octa-2,6-dienyloxycarbonyl)-ethyl]-hexyl ester hex-3Z-enyl ester was prepared from 4-hydroxy-nonanoic acid 3,7-dimethyl-octa-2,6-dienyl ester, 2-chlorocarbonic-propionic acid hex-3Z-enyl ester and pyridine.

Example 474-[1-[2-(1,1,5-trimethyl-hexyloxycarbonyl)-ethyl]octyloxycarbonyloxy]-decanoic acid 1,1,5-trimethyl-hexyl ester

5 [0087] To a mixture of 3 g 4-hydroxy-decanoic acid 1,1,5-trimethyl-hexyl ester and 0.75 g pyridine was slowly added 2.5 ml of a 20% solution of phosgene in toluene. The mixture was stirred for 16 hours at room temperature. Water was added and the mixture extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate, 2N hydrochloric acid, water and dried and evaporated to dryness. The residue was chromatographed on silica gel to give 1.9 g of a colourless liquid.

10 NMR (CDCl_3):
 δ 4.71 (quint, 2H), 2.29 (m, 4H), 1.88 (m, 4H), 1.71-1.42 (m, 12H), 1.42 (s, 12H), 1.39-1.08 (m, 22H), 1.88 (d, 18H) ppm.

Example 484-Hex-3-enyloxycarbonyloxy-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester

15 [0088] According to the procedure of Example 34, 4-hex-3-enyloxycarbonyloxy-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester was prepared from 4-hydroxy-undecanoic acid 3-(4-*tert*-butyl-phenyl)-2-methyl-propenyl ester, pyridine and chlorocarbonic acid hex-3-enyl ester (K. F. Podraza, J. Heterocycl. Chem. 1984, 21(4), 1197).

Example 49Carbonic acid 1-(2-dodecylcarbamoyl-ethyl)-octyl ester hex-3-enyl ester

20 [0089] According to the procedure of Example 34, carbonic acid 1-(2-dodecylcarbamoyl-ethyl)-octyl ester hex-3-enyl ester was prepared from 4-hydroxy-undecanoic acid dodecylamide, pyridine and chlorocarbonic acid hex-3-enyl ester (K. F. Podraza, J. Heterocycl. Chem. 1984, 21(4), 1197).

Example 50(E)-3-(2-Hydroxy-phenyl)-acrylic acid 1-(2-hex-3Z-enyloxycarbonyl-ethyl)-hexyl ester

25 [0090] To a solution of 6.14 g 3-[2-(*tert*-butyl-dimethylsilyloxy)-phenyl]-acrylic acid 1-(2-hex-3-enyloxycarbonyl-ethyl)-hexyl ester in 50 ml of tetrahydrofuran, a solution of 25 ml of a 1M tetrabutylammoniumfluoride solution was dropped in at 0°C. After stirring at room temperature for 90 minutes, the solution was quenched with water and extracted with ether. The organic phase was washed with water, dried and evaporated to dryness. The residue was purified by Kugelrohr-distillation and chromatography to yield 0.51 g of a colourless oil.

NMR (CDCl_3):
 δ 8.01-7.85 (d, 1H), 7.40-7.23 (m, 3H), 6.85-6.71 (m, 2H), 6.60-6.45 (d, 1H), 5.52-5.08 (m, 2H), 5.06-4.88 (m, 1H), 4.05-3.89 (t, 2H), 2.44-2.12 (m, 4H), 2.10-1.68 (m, 4H), 1.67-1.00 (m, 8H), 0.98-0.68 (m, 6H) ppm.

Example 51

45 [0091] Test cloth was washed with a lipase-containing detergent to which one or more of the precursors of Examples 16 to 50 had been added. Headspace analysis of the wet and dry laundry indicated the presence of the fragrances. The fragrance level was higher than when the test cloth was washed with a lipase-containing detergent to which one or more fragrances were added.

Example 52

50 [0092] Test cloth was washed with a lipase-containing detergent and then a fabric softener, containing one or more of the precursors of Examples 16 to 50 was added to the rinse cycle. The laundry was then line-dried. Headspace analysis of the wet and dry laundry indicated the presence of the fragrances. The fragrance level was higher, especially in the dry phase, than when the test cloth was washed with a lipase-containing detergent and then a fabric softener, containing one or more fragrances, was added to the rinse cycle.

Example 53

[0093] Test cloth was washed with a detergent and then a fabric softener, containing one or more of the precursors of Examples 16 to 50 was added to the rinse cycle. The laundry was then tumble-dried. Headspace analysis of the wet and dry laundry indicated the presence of the fragrances. The fragrance level was higher, especially in the dry phase, than when the test cloth was washed with a detergent and then a fabric softener, containing one or more fragrances, was added to the rinse cycle.

Example 54

[0094] Axilla bacteria cultures containing 0.1 % of one or more of the precursors of Examples 16 to 50 were incubated for 20 hours at 30 °C. After filtration from the cells, the presence of the corresponding fragrance was in each case detected by headspace-GC techniques and/or the majority of an 18 member panel.

[0095] The same tests were carried out with inactivated cultures (85°/20 min). The odour of the corresponding fragrance could not be detected after incubation, excluding therefore a hydrolysis by the medium or the culture.

[0096] The following set forth examples for the use of the compounds of the present invention in various products. The methods of forming the following compositions are well known to those skilled in the art. All formulations may contain additional ingredients known to those skilled in the art, e.g. colorants, opacifiers, buffers, antioxidants, vitamins, emulsifiers, UV absorbers, silicones and the like. All products can also be buffered to the desired pH. All values are % w/w. Delayed Release Fragrances stands in the following for compounds of Examples 16-50.

Example 55[0097]

a) Deo-colognes					
Delayed Release Fragrances	0.5	1.5	2.5	6.0	
Fragrance	0.5	1.5	2.5	6.0	
Triclosan (Ciba Geigy)	1.0	-	0.75	1.0	
Alcohol to	100	100	100	100	

b) Deo-Sticks		
Antiperspirant		
Ethylene Glycol Monostearate		7.0
Shea butter		3.0
Neobee 1053 (PVO International)		12.0
Generol 122 (Henkel)		5.0
Kesscowax B (Akzo)		17.0
Dimethicone Dow Corning 345		35.0
Aluminum Sesquichlorhydrate		20.0
Delayed Release Fragrances		0.5
Fragrance		0.5
Antiperspirant		
Steary Alcohol		17.0
Castor Wax		3.0
Talc		5.0
Aluminum Zirconium Tetrachlorhydrate		20.0
Delayed Release Fragrances		1.0
Fragrance		1.0
Dimethicone Dow 245		to 100.0

(continued)

Clear Deodorant Stick	
5	Witconol APM 43.0
	Propylene Glycol 20.0
	Alcohol 39C 20.0
	Demin water 7.0
10	Monamid 150ADD 5.0
	Millithix 925 2.0
	Ottasept Extra 0.5
	Delayed Release Fragrances 0.75
	Fragrance 0.75
15	Deodorant Stick
	Propylene Glycol 69.0
	Demin Water 21.8
20	Triclosan 0.2
	Sodium Stearate 8.0
	Delayed Release Fragrances 0.5
	Fragrance 0.5
25	Alcohol free Deodorant Stick
	PPG-3 Myristyl Ether(Witconol APM) 36.0
	Propylene Glycol 36.0
	Demin Water 19.0
30	Triclosan 0.25
	Sodium Stearate 7.75
	Delayed Release Fragrances 0.5
	Fragrance 0.5
35	Antiperspirant Aerosol
	Absolute Ethanol 15.0
	Zirconium Aluminum tetrachlorhydrate 5.0
40	Bentone 38 1.5
	Delayed Release Fragrances 0.75
	Fragrance 0.75
	S-31 Hydrocarbon propellant to 100.0
45	Antiperspirant Pump
	Demin water 57.5
	Aluminum Sesquichlorhydrate 20.0
50	Triton X-102 (Union Carbide) 2.0
	Dimethyl Isosorbide (ICI) 20.0
	Delayed Release Fragrances 0.25
	Fragrance 0.25
55	Roll-On
	Dimethicone DC 354 (Dow Corning) 69.0
	Bentone 38 10.0

(continued)

5	Roll-On	
	Rezal 36 GP (Reheis Chem. Co.)	20.0
	Delayed Release Fragrances	0.5
	Fragrance	0.5

[0098] In the above examples, the following components were used:

10	Triclosan	5-chloro-2- (2,4-dichlorophenoxy)phenol
	Neobee 1053	glycerol tricaprate/caprylate
	Generol 122	soya sterol
	Kesscowax B	cetyl alcohol and glycol polymer
15	Witconol APM	polypropylene glycol-3 myristyl ether
	Monamid 150 ADD	cocoamide diethanolamine
	Millithix 925	dibenzylidene sorbitol
	Ottasept Extra	quaternium 18 hectorite
20	Bentone 38	quaternium 18 hectorite
	Triton X-102	octoxynol-13
	Dimethicone DC 354	mixture of fully methylated linear siloxanopolymers end-blocked with trimethylsiloxy units
	Rezal 36 GP	Aluminium zirconium tetra-chlorohydrexglycine

25 Example 56

[0099]

30	a) Fabric softener of the ester quat type (4 x concentrate):		
	INGREDIENTS	CHEMICAL NAME	
	PHASE A		
35	DEIONISED WATER		
	MgCl ₂ (saturated sol.)	Magnesium chloride	
	PHASE B		
40	REWOQUAT WE 18	Di-(tallow carboxyethyl) hydroxy ethyl methylammonium methosulfate	
	GENAPOL O 100	Ethoxylated fatty alcohol C16-C18 10EO	
	ANTIFOAM DB 31		
45	PHASE C		
	ISOPROPYL ALCOHOL		
	PRESERVATIVE		
50	PERFUME		

PROCESS:

[0100] While stirring and heating to 65° C, mix part A, then part B preheated to 65° C. After cooling to room temperature, add part C.

55 [0101] The PH value of the finished product is 2.60.

[0102] Recommended level of perfume is 1.0 %. Delayed release fragrances can be any part of this 1.0 %.

	b) Fabric softener of the ester quat type (1 x concentrate) :		
	INGREDIENTS	CHEMICAL NAME	%
5	PHASE A		
	DEIONISED WATER		to 100.0
	PHASE B		
10	REWOQUAT WE 18	Di-(tallow carboxyethyl) hydroxy ethyl methyl ammonium methosulfate	6.0
	DOBANOL 25-9	Ethoxylated fatty alcohol C12-C15 9EO	0.5
	ANTIFOAM DB 31		0.1
15	PHASE C		
	MYACIDE BT 30	2-bromo-2-nitropropane 1,3 diol	0.03
	PROXEL GXL	Benzisothiazolinone sodium salt	0.02
20	PERFUME		Qs

PROCESS:

25 [0103] While stirring and heating to 65° C, mix part A, then part B preheated to 65° C. After cooling to room temperature, add part C.
 [0104] The pH value of the finished product is 3.50.
 [0105] Recommended level of perfume: 0.3 %. Delayed release fragrances can be any part of this 0.3 %.

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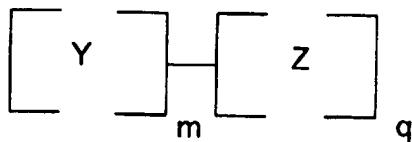
Claims

1. Compounds of Formula I

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I

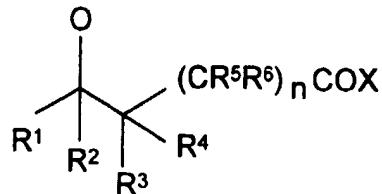
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wherein Y is

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m is an integer of 1 or greater

5 n is 1, 2 or 3;

10 R¹, R², R³, R⁴, R⁵ and R⁶ represent independently hydrogen, substituted or unsubstituted alkyl-, alkenyl-, alkinyl-, cycloalkyl-, cycloalkenyl- or aromatic radicals which can additionally contain one or more -O-and/or

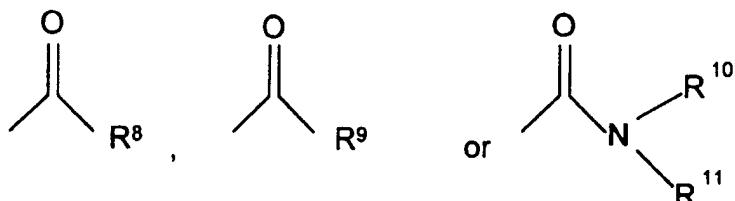
15 O

16 -C-

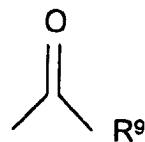
20 groups; whereby one or two rings can be built by the combination of the respective R¹ to R⁶ and said ring(s) can be substituted by one or more alkyl groups;

25 X is -OR⁷ and R⁷ is the residue of an alcohol R⁷OH, or the residue of the enol form of an aldehyde or ketone, or X is a primary, or secondary amino group forming an amide;

30 Z is

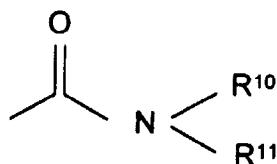


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10 and R⁹ is derived from an organoleptic compound or Y.

10 4. Compound according to claim 1, wherein Z is

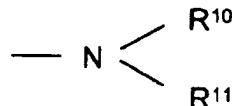
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and

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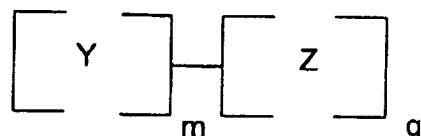
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is derived from a non odorous mono- or diamine.

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5. Compounds according to claim 1 or 2, wherein Z is the residue of a β -keto acid.
 6. Compounds according to claim 1 or 2, wherein

35



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is a photolabile ester.

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7. Compounds of claim 6 yielding under activating conditions, preferably light, an odorous or fluorescent coumarin.
 8. Compounds according to any one of the preceding claims, wherein R⁸ comprises and/or is substituted by one or more

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OCOR⁷, COOR⁷, COY, Si and/or N.

9. Compound according to any one of the preceding claims, wherein R⁹, R¹⁰ and/or R¹¹ comprise and/or are substituted by one or more O, Si, N and/or CO.

10. Compositions comprising a compound of formula I as precursor for at least one organoleptic compound.
11. Laundry compositions according to claim 10 comprising a compound of formula I as precursor for an organoleptic compound and/or a fluorescent coumarin.

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European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 99 81 0249
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	BEILSTEIN INFORMATION SERVICE; FILE: XFIRE, XP002109108 see the attached compounds ---	1-10	C07C69/007 C07C69/96 A61K7/32 A61K7/46
Y	EP 0 816 322 A (GIVAUDAN ROURE INT) 7 January 1998 * the whole document *	1-11	
Y	WO 97 30687 A (GYGAX PETER ;ANDERSON DENISE (CH); FRATER GEORG (CH); GIVAUDAN ROU) 28 August 1997 * the whole document *	1-11	

			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07C A61K
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search MUNICH	Date of completion of the search 14 July 1999	Examiner Goetz, G	
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>4 : member of the same patent family, corresponding document</p>			



Claim(s) searched incompletely:
1-11

Reason for the limitation of the search:

1. The scope of the claims directed to compounds is so broad that a complete search cannot be performed. The only characterizing feature of the claimed compounds is the fact that a part "Y" is connected to a carbonyl-group (see definition of "Z"). The only characterizing feature of "Y" is that an ether-group is connected to a carboxy-group (COX) via a linking group which consists of 3 to 5 carbon atoms which can be unlimited substituted. The performed incomplete search revealed such a large number of compounds falling within the scope of the present claims that the drafting of a comprehensive European Search Report is not feasible. The cited document (see Beilstein Information Service) gives just a small selection of compounds which are novelty-destroying for the present claims directed to compounds.
2. When reading present claims in the light of the description doubts arise concerning the extent of protection afforded by the claims, thus rendering the claims unclear contrary to Article 84 EPC: present examples 1 to 27 do not fall within the scope of present claim 1 because the characterizing features mentioned under point 1 are not met.
3. There is no definition to be found for "R7" nor "R12" (see claim 1 page 54) in any of the claims nor in the description.
4. The definitions for "R8" (claim 2), "R9" (claim 3), "Z" (claim 4) are unclear and subjective and render thus the whole claim unclear (Article 84 EPC).
5. Claim 7 and 10 are characterized by the intended result to be achieved (Article 84 EPC).

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 81 0249

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-07-1999

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		AU 3221697 A	21-01-1998
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